# POLYLACTIDES. A NEW ERA OF BIODEGRADABLE POLYMERS FOR PACKAGING APPLICATION

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## Abstract

Polylactide polymers have garnered enormous attention as a replacement for conventional synthetic packaging materials since they are biodegradable, compostable, and recyclable. In this study, commercially available PLA films, bottles, and trays were evaluated. PLA films show better ultraviolet light barrier properties than polyethylene, but were slightly worse than polystyrene (PS) and polyethylene terephthalate (PET). PLA films show better mechanical properties than PS, and comparable to those of PET. PLA has lower melting and glass transition temperature than PET and PS. Solubility parameter predictions indicate that PLA will interact with nitrogen compounds, anhydrides, and some alcohols, and it will not interact with aromatic hydrocarbons, ketones, esters, and water. In terms of barrier, PLA showed $O_2$ and $CO_2$ permeability coefficients lower than PS and higher than PET. The amount of lactic acid and its derivatives that migrate to food simulant solutions from PLA was much lower than any of the current average dietary lactic acid intake values reported by governmental organizations.

## 1. Introduction

Poly(lactide), PLA, polymers have been used as packaging materials in the last few years, meanly as containers for deli/convenience, dairy, bakery and fresh food products. As modern technologies are lowering the production costs, PLA has becoming an increasing alternative for a broad array of products and is available for new packaging applications.[1-3] Currently commercial PLA polymers are fabricated by polymerizing lactic acid monomer (LA). Polymerization through lactide (L) formation is by and large the current method use for producing massive quantities of PLA polymers. In this method, either D-lactic acid (DLA), L-lactic acid (LLA), or a mixture of the two are pre-polymerized to obtain an intermediate low molecular mass PLA), which is then depolymerized into a mixture of lactide stereoisomers. Lactide (L) is formed by the condensation of two lactic acid molecules as follows: L-lactide (two L-Lactic acid molecules) (LLL), D-lactide (two D-Lactic acid molecules) (DDL), and meso-lactide (an L-lactic acid and a D-lactic acid molecule) (LDL). After purification the lactides are polymerized into high molecular mass PLA with a constitutional unit of $–[OCH(CH_3)CO\text{-}O\text{-}CH(CH_3)\text{-}CO]$-.[4]

Properties of PLA such as melting point, mechanical strength, and crystallinity are determined by the polymer architecture (i.e., proportions of LLL, DLL or LDL) and the molecular mass (i.e., proper addition of hydroxylic compounds). As for other plastics, final user properties of PLA also depend on compounding and processing conditions. The proportion of D and L lactides determines polymer morphology, and PLA can be produced totally amorphous or up to 40% crystalline. This results in PLA polymers with a wide range of hardness and stiffness values. The glass transition temperature of PLA ($T_g$) ranges from 50ºC to 80ºC while the melting temperature ($T_m$) ranges from 130ºC to 180ºC.

Due to its interesting physical and mechanical properties and its hydrolysis and degradation when exposed to heat and humidity, poly(lactide) is a good candidate for packaging applications.[5] PLA is totally degraded in aerobic or anaerobic environments in two months to five years, and early chain fragmentation can be obtained at higher humidity and temperature in composting facilities as soon as fifteen days.

Since the use of PLA is increasing as a food packaging polymer for short shelf life products with common applications such as containers, drinking cups, sundae and salad cups, overwrap and lamination films, and blister packages, there is a main concern to assess how PLA performs under real and differing environmental conditions (i.e., refrigerated, standard, and tropical). The aim of this research was to study the performance of PLA films, bottles, and trays under different environmental conditions, and compare these results with standard synthetic polymers such as PET and PS.

## 2. Materials and Methods

Two poly(lactide) films identified as 98% L-lactide (PLA98L) and 94% L-lactide (PLA94L) were provided by Cargill-Dow LLC Polymers; densities were 1,240 $kg/m^3 \pm 0.002$ and 1,243 $\pm$ 0.002 $kg/m^3$, respectively. Films were studied as received. Thickness of films was determined with a TMI 549M micrometer caliper (Testing Machines, Inc., Amityville, NY) according to ASTM D374 – 99. PET, PS, Cellophane (CE), and low density polyethylene (LDPE) films and PET and PS bottles and trays were used for comparison. PLA bottles were provided by Kraft foods.

*Optical Properties.* Light transmission in the UV and visible range was determined with a Perkin Elmer Lambda 25 UV/VIS Spectrometer with an RSA-PE-020 integrating sphere (Wellesley, MA). Color of the samples was determined by a ColorQuest system from Hunter Lab, (Reston, VA). The yellowness index was calculated according to $YI=100(C_xX-C_zZ)/Y$, where $C_x=1.2769$ and $C_z=1.0592$ according to ASTM D 6290-98e1.

*Physical Properties*. A differential scanning calorimeter (DSC) from TA Instruments (New Castle, DE) was used to determine glass transition ($T_g$) and melting temperature ($T_m$) (ASTM D3418–97); enthalpies of fusion ($\Delta H_f$), and crystallinity of polymers ($\chi_C$) (ASTM D3417–97).

*Mechanical Properties*. Tensile properties of the polymers were determined by an Instron 4201 from Instrom, (Canton, MA) according to ASTM D882-02[1]. Impact strength of PLA98L and PLA94L films were determined by the free falling dart method according to ASTM D1709-98 method A at 25ºC. The crush resistance of rigid PLA and PET bottles and trays was measured by a compression test according to ASTM D2695-95 (2001).

*Barrier Properties.* Oxygen barrier transmission rate was measured according to ASTM D3985-02e1 with an Oxtran 100/Twin. Carbon dioxide transmission rate was measured with a Permatran C-IV, and water vapor transmission rate was measured according to ASTM F1249-90(1995) with a Permatran W3/31. All the equipment was from MOCON Inc (Minneapolis, MN).

*Solubility*. Regular solution theory (RST) was used to predict the solubility of PLA, PET, and PS polymers in different chemical compounds. A two dimensional plot of $\delta_v^2= \delta_d^2+\delta_p^2$ versus $\delta_h$ was used to indicate the interaction region between the polymers and the solvents. $\delta_d$, $\delta_p$, and $\delta_h$ are the non-polar interaction, polar interaction, and hydrogen bonding contribution of the Hansen solubility parameters, respectively. The predictions were done at 25ºC.

*Migration*. Total migration was determined for PLA98L films at 40ºC and for 15 days according to ASTM-4758-98[3] and Food and Drug Administration (FDA) regulations. 10% ethanol and 95% ethanol v/v were used as simulant solutions. 10% ethanol is a simulant for aqueous and acidic foods, and 95% ethanol is a simulant for fatty food products.

## 3. Results & Discussion

PLA98L and PLA94L are glossy and clear polymer films with similarities to PS films. The thickness of the PLA98L was 23.2 µm (0.92 mil) and for PLA94L was 28.5 µm (1.12 mil).

*Optical Properties.* Figure 1 shows the transmission rate versus the wavelength for PLA, PET, PS, LDPE, and CE films. PLA polymers are better UV C barriers than LDPE but slightly worse than PS, CE, and PET. Similar results were found for the containers. PLA containers should be protected against UV light when the product requires. Figure 2 shows the color difference ($\Delta E^*ab$) according to the CIELAB system. The CIELAB system can be visualized as a cylindrical coordinate system in which the axis of the cylinder is the lightness variable $L^*$, ranging from 0% to 100%, and the radii are the chromaticity variables $a^*$ and $b^*$. Variable $a^*$ changes from green (negative) to red (positive), and variable $b^*$ changes from blue (negative) to yellow (positive). LDPE and PS are more similar in appearance to PLA than CE and PET. PLA98L, CE, PS, LDPE, and PET show a yellowness index of 4.67, 6.30, 4.32, 4.67, and 5.71, respectively. PLA film has a refractive index of $\eta=1.482$, similar to LDPE. [6]

*Physical Properties*. Table 1 shows the $T_g$, $T_m$, and $\chi_C$ for PLA98L, PLA94L, PS, and PET. PLA98L and 94L undergo an endothermic event superimposed on $T_g$, which is observed during the first DSC heating. This endothermic relaxation, with an average enthalpy of 1.4 J/g, results from a secondary molecular reordering undergone in the amorphous phase of semi-crystalline polymers. The endothermic peak is eliminated as the sample is heated above $T_g$. PLA98L and 94L show a lower $T_g$ than PS and PET. PLA98L has a higher $T_g$ than PLA94L due to the higher L-lactide content. The lower $T_g$ and $T_m$ values make PLA easy to seal and to process.

*Mechanical Properties*. Figure 3 shows the tensile properties of PLA98L, PLA94L, PS and PET. PLA94L shows a higher tensile yield stress than PLA98L. The tensile strength values obtained for PLA98L and 94L are within the range of values of PS, but they are lower than PET. PLA could be compared to PS and PET samples. PLA98L shows a higher impact failure of (360g) compared with PLA94L (175g). Since the tests were done at room temperature, which is under the $T_g$ values of the samples, and PLA94L has a higher content of amorphous content, it is expected to fail at a lower weight than PLA98L. PET bottles and trays showed higher peak load values than PLA bottles and trays (results not shown here).

*Barrier Properties.* Oxygen and carbon dioxide permeability coefficient of PLA94L, PLA98L, PET, and PS films are presented in Figure 4. PLA shows better oxygen and carbon dioxide barrier properties compared with PS, but lower than PET. Carbon dioxide barrier properties are around four times lower than oxygen barrier properties for PLA94L and PLA98L. Figure 5 shows the water vapor permeability coefficients of PLA94L, PLA98L, PET and PS films. PLA films show lower water barrier properties than PS and PET. Values of PLA98L oxygen, carbon dioxide and water permeability activation energy were reported as 30.30 kJ/mol (0% RH), 15.65 kJ/mol (0% RH), and -10 kJ/mol (100% RH), respectively.[7]

*Solubility*. Regular solution theory (RST) prediction indicates that PLA polymers may be dissolved in nitrogen compounds, anhydrides, and some alcohols, and it may not be dissolved in aromatic hydrocarbons, ketones, esters, and water at room temperature. Figure 6 shows the tentative regions of interactions for alcohols. Compounds that are contained inside the circles may dissolve PLA polymers to some degree. Figure 7 shows the predictions for nitrogen compounds. Further studies are necessary to confirm these predictions.

*Migration*. Migrants from PLA may include lactic acid, lactide, lactoyllactic acid, and its dimer. Lactic acid is the substance of primary interest because the other species are expected ultimately to hydrolyse to lactic acid. Total migration studies done in PLA98L in 10% ethanol and 95% ethanol simulant solutions are presented in Figure 8. This figure shows that the amount of lactic acid and its derivates that migrates to the ethanol solution (i.e., 10% and 95% ethanol) from PLA98L are much lower than any of the current dietary lactic acid intakes values reported by the FDA. These results are in agreement with previous findings. [8]

## 4. Conclusions

PLA are economically feasible materials to use as packaging polymers. They provide consumers with extra end-use benefits such as compostability, recyclability, and renewability. In this study the optical, physical, mechanical, and barrier properties of PLA98L and PLA94L were studied and compared with commercially available synthetic polymers (PET and PS). Total migration studies were carried out in simulant solutions.

Poly(lactide) films and containers have optical properties similar to LDPE and PS polymers, and for demanding applications they can be improved with pigment and blocking agents. PLA films and containers have a slight natural yellow color when compared with PS and PET. PLA98L and PLA94L have lower $T_g$ and $T_m$ than PET and PS, which makes PLA better for heat sealing and thermal processing. Mechanical properties of PLA are comparable to PS, and in many cases are better. Oxygen and carbon dioxide permeability coefficients of PLA are lower than PS and higher than PET. Water permeability coefficients of PLA are higher than PS and PET. RST indicates that PLA may be partly or totally dissolved in nitrogen compounds, anhydrides, and some alcohols. Aroma barrier properties of PLA polymers are comparable to PET and much better than PS. Total migration studies indicated that the amount of lactic acid and its derivatives that migrate to 10% ethanol and 95% ethanol solutions are lower than any of the current dietary lactic acid intakes values reported by the FDA.

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## Keywords

Poly(lactide); barrier; migration; solubility.

**Table 1**. Physical properties of PLA98L, PLA94L, PS and PET

| | **PLA98L** | **PLA94L** | **PS** (atactic)* | **PET** |
|---|---|---|---|---|
| $T_g$, ºC | 71.4 | 66.1 | 100 | 80 |
| $T_m$, ºC | 163.4 | 140.8 | N/A | 245 |
| Enthalpy of Fusion, J/g | 37.5 | 21.9 | N/A | 47.7 |
| Percent Crystallinity | 40 | 25 | N/A | 38 |

*PS used in packaging is atactic, so it does not crystallize. Since it is an amorphous polymer, it does not have a defined melting point, but gradually softens through a wide range of temperatures

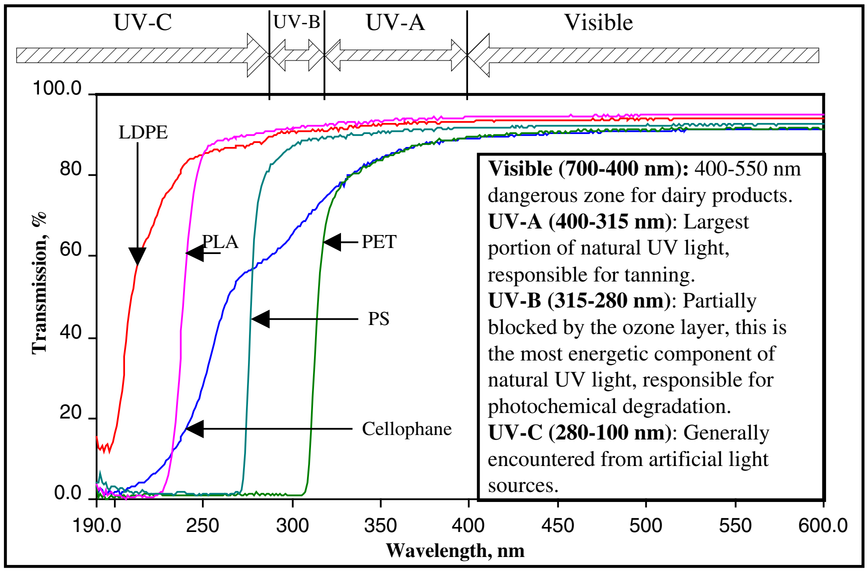



**Figure 1**. % transmission versus wavelength for PLA98L, PS, LDPE, PET and CE films.

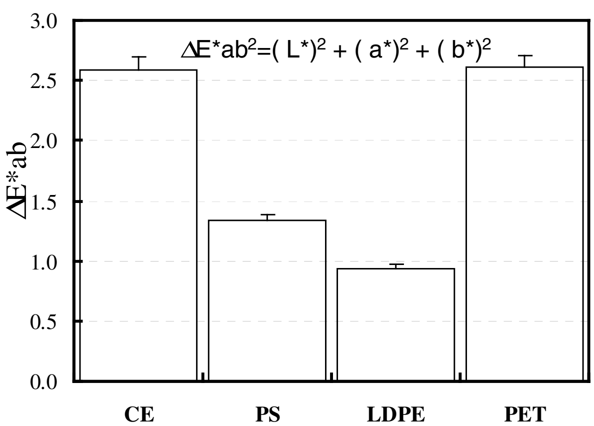



**Figure 2.** $\Delta E^*ab$ values for PLA, CE, PS, LDPE, PET, and CE films. L* is the lightness, and a* and b* the radii of chromaticity.

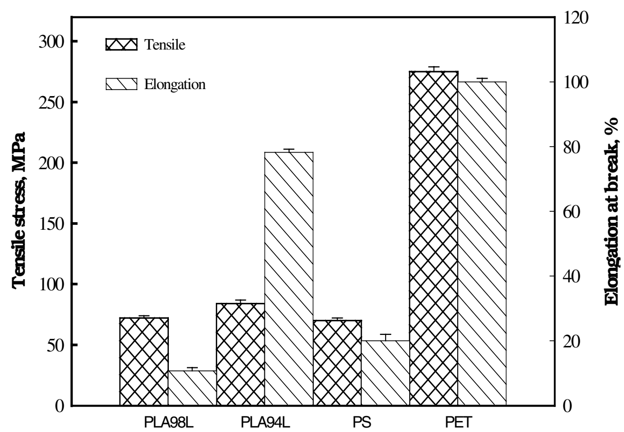



**Figure 3.** Tensile stress and Elongation at break of PLA98L, PLA94L, PS and PET

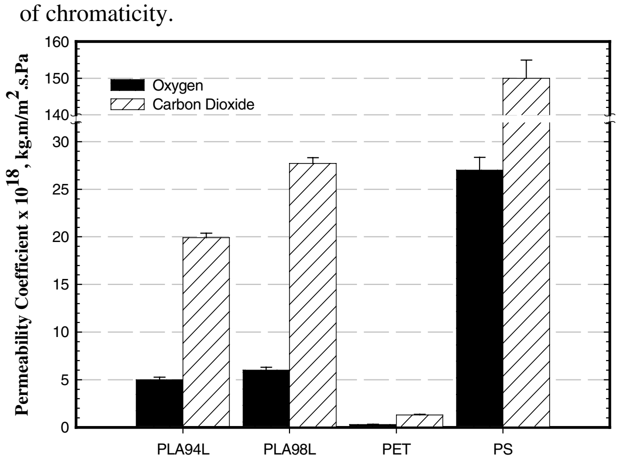



**Figure 4.** Oxygen and Carbon Dioxide Permeability Coeffic ients of PLA94L, PLA98L, PS and PET at 25ºC and 0% RH.

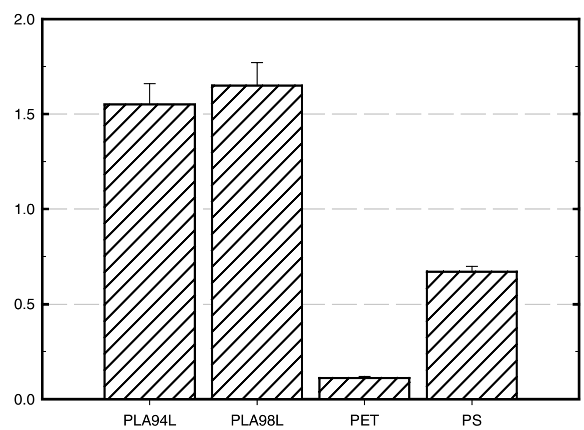



**Figure 5.** Water Vapor Permeability Coefficients of PLA94L, PLA98L, PS and PET at 30ºC and 100%RH

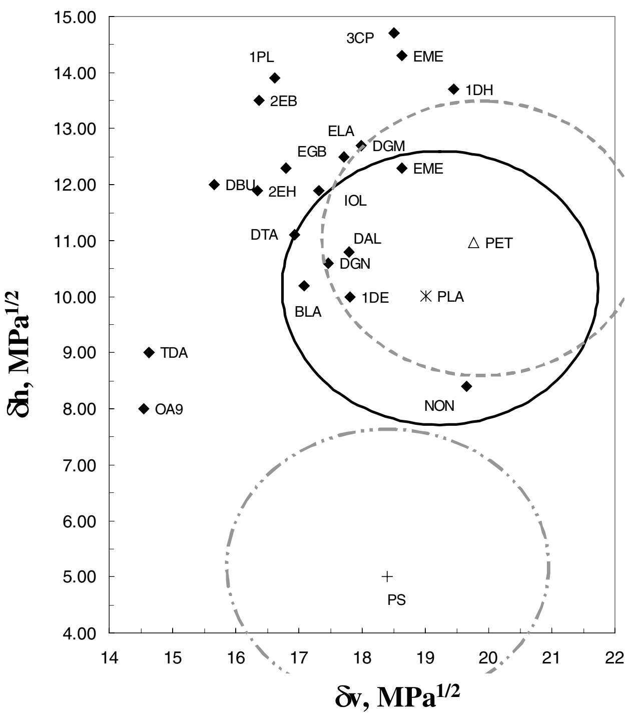



**Figure 6**. Volume dependent cohesion parameter ( δv) vs Hansen hydrogen bonding parameter for Poly(lactide) and Alcohol. Values indicated for solvents with Δδ<5 MPa1/2 . (3CP, 3-Chloropropanol; BEA, Benzyl alcohol; CHL, Cyclohexanol; 1PL, 1-Pentanol; 2EB, 2-Ethyl-1-butanol; DAL, Diacetone alcohol; DBU, 1,3- Dimethyl-1-butanol; ELA, Ethyl lactate; BLA, n-Butyl lactate; EME, Ethylene glycol monotethyl ether; DGM, Diethylene glycol monoethyl ether, methyl; DGE, Diethylene glycol monoethyl ether, EGB, Ethylene glycol mono-n-butyl ether; 2EH, 2-Ethyl-1-hexanol; IOL, 1-Octanol; 2OL, 2-Octanol; DGN, Diethylene Glycol mono-n-butyl ether; 1DE, 1-Decanol; TDA, 1-tridecanol; NON, Nonyl; OA9, Oleyl alcohol)

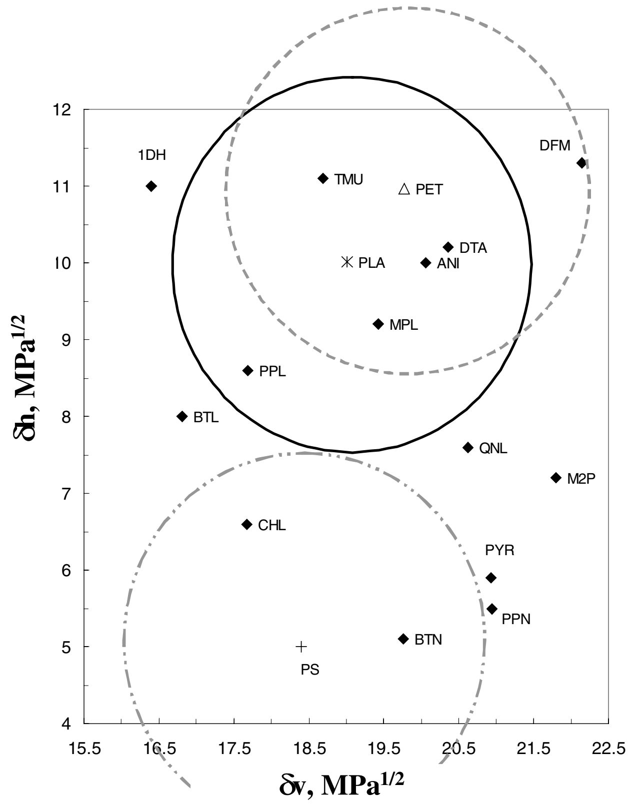
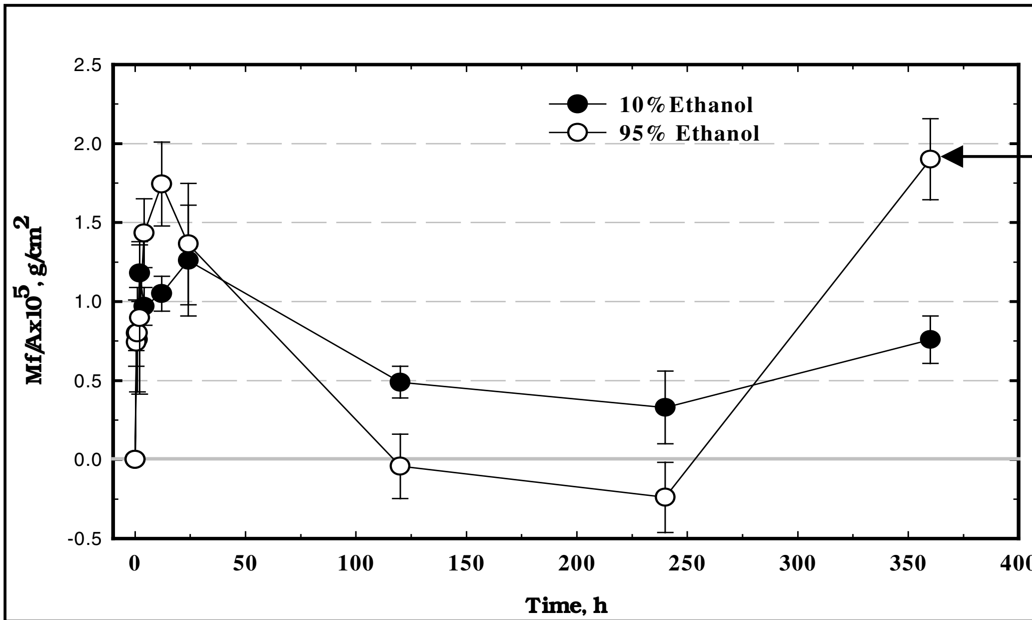



**Figure 7**. Volume dependent cohesion parameter (δv) vs Hansen hydrogen bonding parameter for Poly(lactide) and Nitrogen Compounds. Values indicated for solvents with Δδ<5 MPa $^{1/2}$ . ( PPN, Propionitrile; BTN, Butyronitrile; 1DH, 1,1,-Dimethylhydrazine; PYR, Pyridine; PPL, n-Propylamine; MPL, Morpholine; ANI, Aniline; M2P, N-Methyl-2-Pyrrolidone; BTL, n-Butylamine; CHL, Cyclohexylamine; DFM, N,N-Dimethylformamide; DTA, N,N-Dimethylacetamide; TMU, Tetramethylurea)




The total amount of lactic acid that migrated to the 95% Ethanol simulant solution at 15 days (360 h) and 45ºC (i.e., $2.0x10^{-5}$ g/cm²), is equivalent to a total migration of 12.9 mg/kg of food in contact with the film. Calculation done according to FDA guideline (i.e., 10 g of food in contact with each square inch of packaging surface).

**Figure 8**. Mass migrated into the food per unit of area of polymer in g/cm2 versus time. Simulant solutions 10% Ethanol and 95% Ethanol. The gray line indicates the zero baseline.